

# The Hardness of Aluminum Oxide Surface in Anodized Coloring Under Low Voltage

Haris Puspito Buwono<sup>1a</sup>, Syamsul Hadi<sup>1</sup>, Mochamad Muzaki<sup>1</sup>, Subagiyo<sup>1</sup>, Lisa Agustriyana,<sup>1</sup> Samsul Hadi,<sup>1</sup> and Nurchajat<sup>1</sup>

<sup>1</sup>Mechanical Engineering Department, Politeknik Negeri Malang, Jl. Soekarno-Hatta No. 9 Malang, Jawa Timur, 65141

<sup>a</sup>Corresponding author: [haris.puspito@polinema.ac.id](mailto:haris.puspito@polinema.ac.id)



**Abstract**—Coloring of aluminum oxide on the Aluminum type AA1100, which is the typical type for household appliances and purposes, through anodizing coloring process by the blue color of commercial printer ink had been successfully performed. The blue color was well adhered and was not easy to be removed by physical treatment such as wiping. The anodize coloring process includes chemical cleaning of aluminum surface, the formation of pores in the sulfuric acid solution at a specific current and a specified duration of time, coloring and closing the pores via sealing. It also shows the anodizing process increases aluminum oxide surface hardness increased by applying higher current density, and longer duration time of the process. The aluminum oxide hardness was in harmony to the duration of time processing, and current density; however, not in line to a concentration of the solution. The maximum hardness of the aluminum oxide layer obtained is 50 kg/mm<sup>2</sup>. The relation of current density and voltage, the effect of current density and sulfuric acid concentration toward aluminum oxide hardness were analyzed. Moreover, the difference of aluminum oxide hardness of the front side and backside to cathode also discussed.

**Keywords**—anodized coloring, hardness, sulfuric acid, ink printer, hardness difference.

## I. Introduction

Nowadays, aluminum is widely processed by anodizing to obtain the esthetics value and to improve technical requirement. It is applied in various household equipment, including kitchen utensils. The color present in the aluminum oxide layer is one of the indicators of the possibility of the metal, or the ion is dissolving/damaging. Interestingly, the color can be used as a degradation parameter. The longer the color remains in the oxide layer, the lower aluminum oxide layer dissolves in the environment; and conversely the faster degradation the color, the more rapid the deterioration of the aluminum layer. This process includes cleaning, the

formation of pores through anodizing, coloring, and sealing.

The process, namely anodizing coloring, is based on controlled corrosion by applying a specific current for a specified time in an electrolytic media. By controlled corrosion, the pores of aluminum formed. So, it is affected by the kinds of electrolytic and its concentration, current density and voltage, duration of time process, and temperature. Before anodizing or controlled corrosion performed, the aluminum surface should be clean to meet criteria. Usually, there are two kinds of cleaning treatment; chemical cleaning, a combination of mechanical and chemical cleaning, and combination of mechanical, chemical and electro-cleaning. The cleaning process should be performed carefully to removed oil, rust, oxide, and to gain a smooth surface. Therefore, this process uses direct current electricity; by giving a negative charge to the companion electrode and a positive charge to the workpiece (of aluminum). Usually, the negative electrodes (cathode) are aluminum. The reaction that takes place at the negative pole is reduction while the positive pole is oxidation. The specimen is placed in the positive pole.

Generally, for decoration applications, the thickness of the oxide film layer is 5-10  $\mu\text{m}$ , for complex architectural, it requires at least 25  $\mu\text{m}$ , and for hard anodizing, its thickness is 25 - 125  $\mu\text{m}$ . Generally, the depth of aluminum oxide was determined by the duration of the anodizing process. The thickness of the oxide layer increases with increasing time and reach 8-10  $\mu\text{m}$  as voltage increases from 20 V into 35 V [1]. The

thickness of the aluminum oxide layer increases linearly with the duration of the anodizing process, and each type of aluminum has a different oxide layer formation rate in sulfuric acid solution  $2 \text{ mol L}^{-1}$  at 15 volts [2]. It also determined by temperature as it increases, the aluminum oxide layer increases and reaches a maximum thickness around 33 - 35  $\mu\text{m}$  at a temperature of 30 °C. Above this temperature, the thickness of the aluminum oxide layer tends to drop [3].

The diameter of the pore and porosity were influenced by potential, temperature, and anodizing time. However, many reports investigated anodizing under high voltage [4], [5], [14], [6]–[13], consecutively, the voltage for sulfuric acid, oxalic acid, chromic acid, dan phosphorus acid are 15-22 Volt, 30-100 Volt, 30-100Volt, and 160-195 Volt. The potential affected the distance between the pores and the density of the pores [15], and it increases exponentially as current increases [16], [17]. The effect of current density and sulfuric acid solution concentration on ionization has been investigated by Chung et al. They indicates that the higher the current density used, the higher the aluminum oxide growth rate [18]. By applying high voltage, the aluminum oxide hardness increase. However, high voltage is appropriate for hard anodizing. In the case of hard anodizing, the diameter of the pores is small so that it could not be fulfilled by color.

Therefore, this study examines the possibility of using printer ink to dye aluminum oxide through the anodizing process and analyzing the hardness of aluminum oxide produced.

## II. Research Methodology

The workpiece is aluminum AA1100 in a square 80mm x 20mm x 3mm, of which 60mm x 20mm x 3mm is processed in anodizing coloring by submerged into every solution applied, and the rest used as holder including the hole. The chemical used for making cleaning solutions such as NaOH, HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> and for the formation of pores namely H<sub>2</sub>SO<sub>4</sub> are technical grade and used as received without further purification. Anodizing coloring process involves three parts including chemical cleaning, pores formation, and coloring and sealing. The details of chemical cleaning

consecutively are washing by soap, degreasing in 10% NaOH, 10% HCl. Each process takes 3 minutes. Then submerged in 5% HNO<sub>3</sub> and 80% H<sub>3</sub>PO<sub>4</sub> for 15 minutes. The formation of pores was performed in 20% sulfuric acid under specific current density and duration of time. All these processes were conducted at room temperature. The coloring of aluminum oxides was performed by submerging it in printer ink solution for 15 minutes at 50 °C. The last step is sealing in water.

The anodizing process was performed using single cathode and single anode. The ratio of the cathode to the anode is 1:1, and the distance between the anode and the cathode is 8 cm. The anodizing process was carried out at room temperature (30 °C), without stirring and aeration. The printer ink color blue and commercially available. The test of color stability was performed by mechanical wiping using commercial fabric. The hardness tests were performed under the Brinell method (BHN). The diameter of indenter is 5 mm, the load is 150 kg, and indentation trace was measured by profile projector.

## III. Result and Discussion

### A. Relation of Current Density and Voltage

Figure 1 shows the relationship between current density and voltage at 15% and 20% sulfuric acid. The data shows that the current density increases linearly to the voltage. At the highest current density (0.015 A/cm<sup>2</sup>), the voltage at 15% sulfuric acid solution a little bit higher than those at 20%. These phenomena probably caused by the effect of a high concentration of a solution. As the sulfuric acid concentration higher, the distance of ions smaller so that the ion interaction higher then it will decrease the resistance of solution. As a result, the voltage at higher concentration decrease.

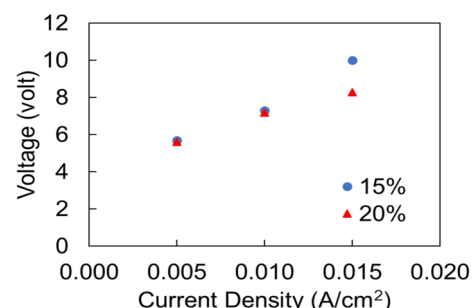


Figure 1. Relation of current density and voltage in 15% and 20% H<sub>2</sub>SO<sub>4</sub>.

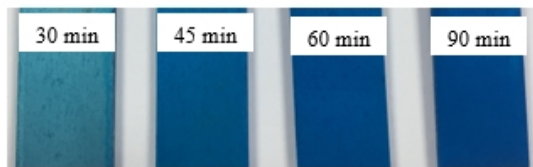


Figure 2. The result of anodizing coloring in 15% sulfuric acid, 0.005 A/cm<sup>2</sup> as time-dependent.

Anodized coloring results can be seen in Figures 2 and 3. Both images show that printer ink can be applied as a dye for the aluminum oxide layer. In the 30 minutes, the colors obtained tend to be slightly lighter than the longer time of anodizing. These are probably due to the processing thickness of pores formed are still thin and not evenly distributed. So, the layer of color tends to be just one layer (monolayer). Whereas for a longer duration time, the pores formed are more evenly distributed and thicker so that the colors can be absorbed better so that it gets a darker layer of color like multi-layers.

All blue colored of anodized aluminums have been tested by mechanical wiping using commercial fabric. The result shows the blue color remains on the surface without any damages. It means that the blue ink printer could be used to colorize the anodized aluminum under low voltage at those conditions.

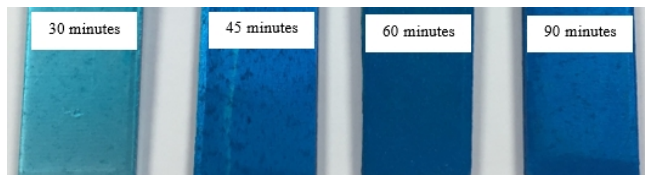


Figure 3. The result of anodizing coloring in 20% sulfuric acid, 0.005 A/cm<sup>2</sup> as time-dependent.

#### B. The Effect of Concentration of Anodizing Solution

The effect of concentration on the hardness of the aluminum oxide layer on the side directly facing the cathode has been investigated, as shown in Figure 4. It shows that the aluminum oxide hardness resulting from the 15% sulfuric acid solution is higher than of it at 20%. The hardness difference of the front side of aluminum oxide (the side that faces directly to cathode) and the backside (the side that faces indirectly to cathode) was observed. Figure 5 and 6 show the hardness difference of the front side and the backside of aluminum oxide. Figure 5 shows the hardness difference of aluminum oxide in 15% sulfuric acid solution. The hardness difference of the aluminum oxide from the anodizing process in a 15%

sulfuric acid solution tends to increase. The longer the duration of the process, the higher the difference in hardness. And the hardness difference of aluminum oxide in the 20% sulfuric acid solution remains too constant as can be seen in Figure 6.

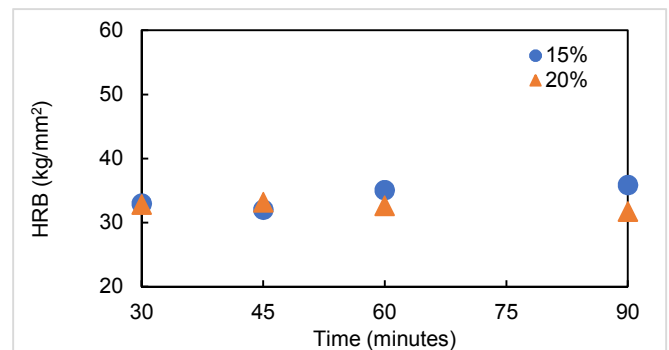


Figure 4. Effect of anodizing time and concentration of sulfuric acid on aluminum oxide hardness at current densities 0.005 A/cm<sup>2</sup>. The concentration of sulfuric acid is 15% and 20%.

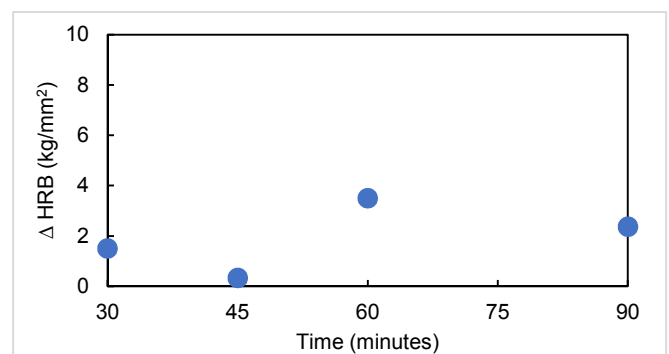


Figure 5. Effect of sulfuric acid concentration on the hardness difference of the aluminum oxide resulted from anodizing coloring on the anode surface which is directly facing and the surface not directly facing cathode in a 15% sulfuric acid solution at a current density of 0.005 A/cm<sup>2</sup>.

Figure 5 and 6 show at concentrations of 15% and 20%, and current densities of 0.005 A/cm<sup>2</sup>, the aluminum oxide layer on the direct-facing side had a higher hardness than the non-direct facing side. Figure 5 shows the hardness difference on side surface forces facing directly and indirectly with the cathode at a 15% sulfuric acid solution concentration. The figure shows that in any concentration range, the hardness of aluminum oxide surface on direct facing to cathode always higher than to its indirect facing cathode. Whereas at a concentration of 20%, the hardness obtained tends to be the same on both sides along with the increase in time, as shown in Figure 6. These are probably caused by the high

concentration of sulfuric acid solution; at 20% sulfuric acid solution the distribution of currents was improved well so that the ionization of aluminum and the formation of pores takes place more evenly.

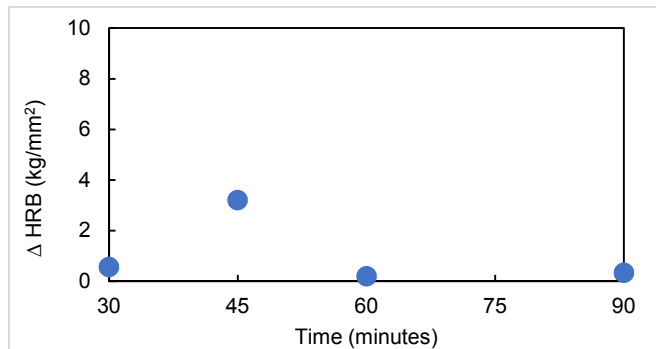


Figure 6. Effect of solution concentration on the hardness difference of the aluminum oxide resulting from anodizing coloring on the anode surface which is directly facing and the anode surface not directly facing cathode in the 20% sulfuric acid solution at the current density of 0.005 A/cm<sup>2</sup>.

### C. The Effect of Current Density

Because the anodizing process in a 15% sulfuric acid solution resulted in a higher level of hardness of the aluminum oxide layer than those in the 20% solution, then higher current density investigated at those concentration to explore the surface hardness of the aluminum oxide. The results are presented in Figure 7. It shows that as current density increase, the surface hardness of the aluminum oxide increase. The maximum hardness is obtained at 50 kg/mm<sup>2</sup>. Interestingly, at the current density of 0.015 A/cm<sup>2</sup>, the longer the duration of the anodizing process the lower hardness; while at the current density of 0.010 A/cm<sup>2</sup>, the longer the duration of the process, the higher the surface hardness and then the constant.

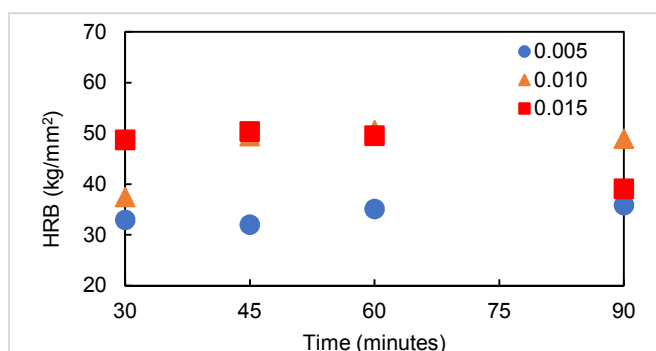


Figure 7. Effect of time and current density on the hardness of the aluminum oxide resulting from anodizing coloring in a 15% sulfuric acid solution. The current densities of the anodizing processes are 0.005, 0.010, and 0.015 A/cm<sup>2</sup>.

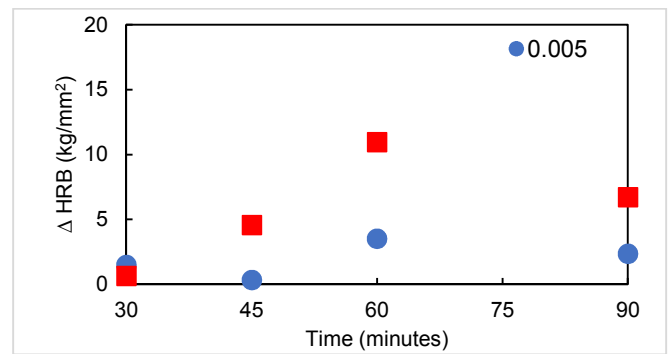


Figure 8. Effect of current density on the hardness difference of the aluminum oxide layer resulting from anodizing coloring on the anode surface which is directly facing and surface which is not directly facing the cathode in a 15% sulfuric acid solution at current density 0.005 and 0.015 A/cm<sup>2</sup>.

The hardness difference between the sides facing directly and indirectly to the cathode (negative pole) is shown in Figure 8. The figure shows that along with the increasing duration/time of the anodizing process, the higher the difference in hardness between the direct and indirect faces. But at a duration of 90 minutes, the hardness difference between the sides facing directly and indirectly suddenly decreases. These phenomena raise speculation that the formation of aluminum pores on the side facing directly to cathode initially faster than it on the side that is not directly facing the cathode. However, at a duration of 90 minutes, the formation of the pore on the face-to-face side might slow down or partially collapse, while on the side that does not face directly the aluminum pores are continued form.

## IV. Conclusion

The coloring on the aluminum surface of AA1100 with printer ink has been successfully carried out through anodizing coloring process. Aluminum oxides surfaces can be colored with a blue printer ink well. The results of simple testing through applying the surface wiping by using cloth show that the color attached to the surface of aluminum oxide is not damaged and can survive well. These show that the aluminum oxide layer has been formed well in the anodizing process, which means the formation of pores has been going well. The size of the pores produced corresponds to the size of the printer ink molecules so that the printer ink molecules can fill these pores and can be locked properly. The results of the study also show linear relations between current and voltage densities. At a higher concentration of a solution, the electrical resistance decreases so that the voltage also decreases. The results also show that the blue color produced is influenced by



the duration of the anodizing process; the longer the duration of the anodization process, the darker the color.

The surface hardness of the aluminum oxide layer produced at 15% sulfuric acid concentration was slightly higher than at 20% concentration. And from the two types of concentration, the hardness of the anode surface directly facing the cathode is always higher than the hardness of the anode surface, which is not directly facing the cathode. However, at a concentration of 20% sulfuric acid solution, the difference in hardness between the sides of the anode facing, directly and indirectly, is smaller than at the concentration of 15% sulfuric acid. These are possibly caused that the ionization process of aluminum is more evenly distributed at higher solution concentrations. Conversely, at a low concentration of the solution, the ionization process is less uniform which results in less uniform pores formed between the front side surfaces (the surface facing cathode directly) and backside (the surface not directly facing the cathode). The maximum hardness of the aluminum oxide is 50 kg/mm<sup>2</sup>.

This study also shows that to increase the surface hardness of the aluminum oxide can be obtained using higher current densities for a maximum of 60 minutes. At high current densities and longer periods, the surface hardness of the aluminum oxide layer tends to decrease. These are probably due to the formed pores collapsing and rearranging.

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